Kerosene space heaters: A major source of ultrafine particles indoors

Olivier Ramalho[1,*], Evelyne Gehin[2], Hervé Guegan[3], Jean Danjou[4], Mickael Derbez[1] and Séverine Kirchner[1]

[1]Building Scientific and Technical Center (CSTB), France
[2]University of Paris 12 - Val de Marne, CERTES, France
[3]Nuclear Research Center of Bordeaux-Gradignan, ARCANE-CENBG, France
[4]Hygiene Laboratory of Paris, LHVP, France

[*]*Corresponding email: olivier.ramalho@cstb.fr*

SUMMARY
Kerosene heaters are known to emit pollutants in the indoor environment but ultrafine particle emission was never reported. A kerosene heater was characterized in an experimental chamber using four different instruments to monitor particle number concentration and size distribution down to 5 nm. Another experiment was realized to collect particles and determine their composition in elements, ions, organic/elemental carbon and polycyclic aromatic hydrocarbons. The kerosene heater produced ultrafine particles in the range 5 to 40 nm with a count median diameter of 9.5 nm. The emission rate was $(1.8\pm0.3)\times10^{11}$ particle·s^{-1}. Chromium and manganese (4 and 0.05 ng·g^{-1} of burned fuel) were specifically associated with kerosene combustion. Trace levels of sulfates, nitrates, phenanthrene and fluoranthene were also detected. Scanning electron microscopy showed submicronic aggregates mostly composed of carbon and traces of silicon. Our findings showed that kerosene heaters represent a major indoor source of ultrafine particles.

KEYWORDS
Ultrafine particles, Kerosene space heater, Chemical analysis, Emission rate, Combustion

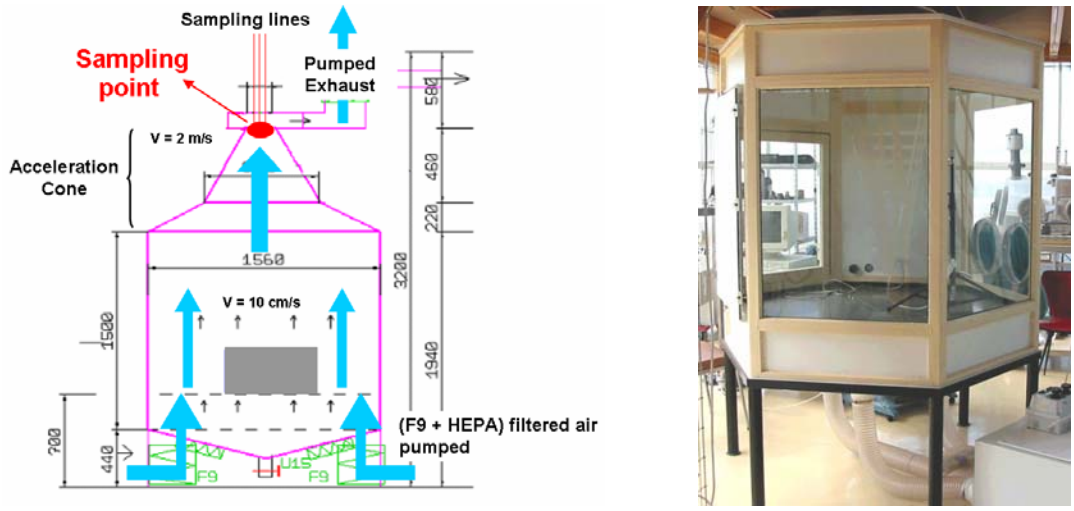
INTRODUCTION
Kerosene space heaters are often used indoors as extra heating in order to minimize energy costs. They are available in the open market and do not require specific knowledge to be installed. Kerosene heaters are known to emit combustion pollutants such as carbon monoxide, sulfur dioxide and nitrogen oxides (Leaderer, 1982; Traynor et al., 1983; Berwick et al., 1989). Chamber experiments conducted by Leaderer et al. (1990) found that fine particulate matter ($PM_{2.5}$) emission rates vary from 30 to 400 µg per gram of burned fuel. Winter investigation in 74 homes with kerosene space heater (a mean of 6.9 hr use on a 24 hr basis) showed an increase in $PM_{2.5}$ and sulfate concentrations by 40 and 15 µg·m^{-3} respectively compared to homes without kerosene heaters (Leaderer et al., 1999). Fan and Zhang (2001) reported no significant change in $PM_{2.5}$ concentrations from the use of a kerosene space heater in a 19 m^3 room. However, measurements with an optical counter (0.1 – 2 µm range in diameter) indicated a low but significant emission of fine particles of 0.1 to 0.2 µm size. This finding suggests that particles below 0.1 µm (i.e. ultrafine particles) may also be emitted but it has never been documented so far.

This paper deals with the chemical and physical characterization of particle emissions in the size range 5 nm to 20 µm resulting from the use of a modern kerosene space heater in an experimental chamber. It is part of a larger study involving the characterization of 20 different domestic activities.

METHODS

A portable kerosene space heater bought in 2005 with a 2,7 kW heating capacity was used in this study. It is suited for a volume ranging between 75 and 95 m^3. The fuel was an organic solvent, a mixture of isoalkanes from 11 to 15 carbon atoms, without odour and containing less than 0.003% of aromatics, <5 $mg \cdot kg^{-1}$ of sulfur and <0.1% of benzene. The device was operated at maximum power during 40 min. The fuel is consumed at a rate of 225 $g \cdot h^{-1}$.

The specifically designed experimental chamber is a 2.36 m^3 volume with glass, stainless steel or plexiglas walls (Figure 1). Gloves through the plexiglas wall allow the handling of devices without disturbing particle concentrations. An HEPA filtered upward flow of 107±2 $m^3 \cdot h^{-1}$ is maintained throughout the experiment. The resulting air exchange rate was 45.5±1 h^{-1} taking into account sampling flowrates from measuring instruments. This high exchange rate minimizes particle interaction with walls and allows an efficient transport of particles to the sampling lines located at the top of the chamber. An upward air velocity of 0.1 $m \cdot s^{-1}$ was measured throughout the chamber height with a low velocity flow analyzer (Dantec Model 54N50). A velocity of 2 $m \cdot s^{-1}$ was achieved at the top of the acceleration cone where particles are sampled. A fan placed just below the acceleration cone area allows a continuous mixing in the sampling zone. The heater is introduced in the chamber through a door on one side. Operating the kerosene heater inside the experimental chamber increases the air temperature from 20 to 50°C and decrease the associated relative humidity from 40 to 10%.



a) Experimental chamber diagram

b) Experimental chamber view

Figure 1. Experimental chamber setup. a) Diagram, b) View.

Measurements were performed with a very fast differential mobility spectrometer (DMS500, Cambustion UK, range 5 – 1000 nm electrical mobility equivalent diameter, 38 channels), an electrical low pressure impactor (ELPI, Dekati, range 0,03 – 10 µm aerodynamic diameter, 12 channels), a condensation particle counter (CPC 3007, TSI inc., range 10 – 1000 nm) and an optical counter (OPC, Dust monitor GRIMM 1.108, range 0,3 – 20 µm optical equivalent diameter, 15 channels). Sampling is performed in near isokinetic conditions through Bev-A-Line XX inert tubing (Thermoplastic Processes) or stainless steel tubing (CPC). Diffusion, inertial, and gravitational losses have been estimated with the Aerosol Calculator Program developped by Paul Baron and based on work by Baron and Willeke (2001). Total losses remain under 15% at the most with CPC in the 10 nm size range. Except for CPC, sampling

efficiency has been taken into account in the following results. A fast acquisition rate of 1 point every second (except OPC, 1 point every 6 s) was selected. Particle number concentration is continuously monitored before, during and after operating the kerosene space heater. Experiments were repeated three times.

Another set of experiments was realized to collect particles on filters in 4 different fractions (< 1 µm, 1-2.5 µm, 2.5-10 µm, > 10 µm) using a 4-stage PM10 Impactor (Dekati) in order to perform several chemical analysis :

- elemental analysis by Particle Induced X-Ray Emission (PIXE, Johansson, 1995) on polycarbonate filter, (7 light elements with 1.5 MeV H^+ beam: Al, Si, P, S, Cl, K, Ca ; 7 elements with 2.5 MeV H^+ beam: Cr, Mn, Fe, Ni, Cu, Zn, Br),
- organic and elemental carbon on quartz filter by oxidative thermal analysis and infrared spectrophotometry,
- anions/cations in the water soluble fraction by capillary electrophoresis on Teflon-coated glass fiber filters, (anions: Cl^-, NO_3^-, NO_2^-, F^-, SO_4^{2-} ; cations: NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+)
- polycyclic aromatic hydrocarbons (PAH) on Teflon-coated glass fiber filters by solvent extraction and liquid chromatography (phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene).

In parallel, total suspended particles were collected on a polycarbonate membrane for characterization by scanning electron microscopy (SEM, Low Vacuum MEB Jeol 5600) equipped with a thin window EDS detector (energy dispersion spectrometry) enabling X-ray detection of carbon and heavier elements.

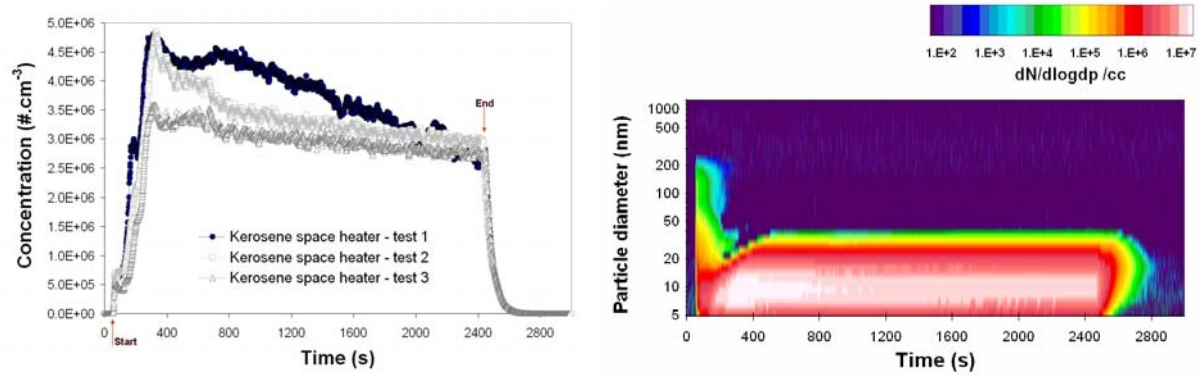
In order to achieve significant particulate matter to realize chemical characterization, 11 heating cycles were performed for a total cumulated duration of 234 minutes and 877.5 g of burned fuel. Sampling duration was 582 min with a total sample volume of 5.7 m^3 (flowrate of 9.7 $L \cdot min^{-1}$) for each chemical analysis. Sample volume for SEM characterization was 2.5 m^3.

RESULTS

Particle number measurements

Background particle concentration in the experimental chamber was at the most below 200 cm^{-3} for 5 nm particles, level in the same order of magnitude than electrical noise from instruments. Mean background level was systematically subtracted from results.

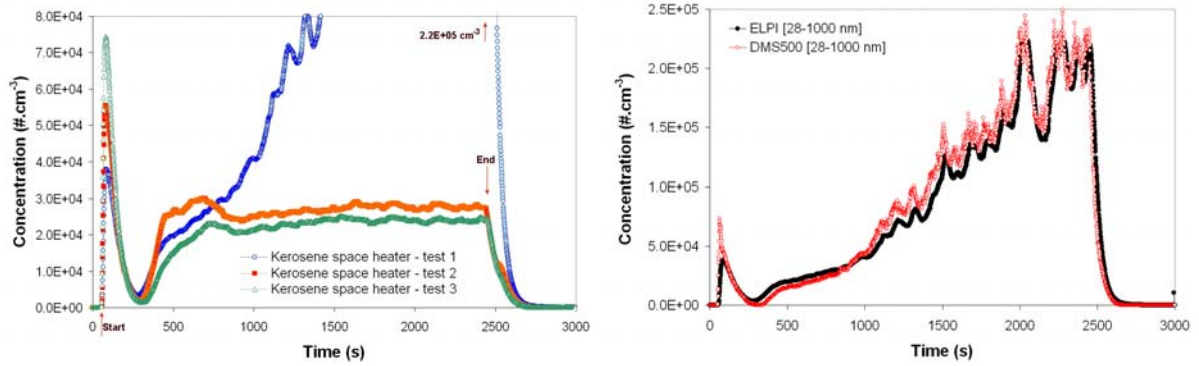
The kerosene space heater produces ultrafine combustion particles in the size range 5 to 40 nm. Ultrafine particle concentration achieved a steady-state level around 3×10^6 particle$\cdot cm^{-3}$ (Figure 2a). The count median diameter (CMD) was 9.5 nm with a geometric standard deviation σ_g of 1.45. The particle size distribution remained constant throughout the heater operation (Figure 2b).



a) Total particle concentration (DMS500) b) Evolution of the particle size distribution

Figure 2. Evolution of total particle concentration (size 5-1000 nm) in the experimental chamber measured with the differential mobility spectrometer. a) Particle concentration, b) Particle size distribution (test 2).

Measurements with the electrical low pressure impactor produce different concentration profiles (Figure 3a). After a first peak in particle concentration associated with the ignition of the heater, the concentration steadies itself after 8 min around a constant value of 2.5×10^4 particle·cm^{-3}. During test 1 however, the concentration continues to increase. It was the first use of the heater and the flame was too high resulting in a poor combustion and emission of larger particles (between 30 and 100 nm). Focusing on these larger particles, a very satisfactory agreement was found between the DMS and the ELPI measurements (Figure 3b).



a) Total particle concentration (ELPI) b) Comparison of ELPI and DMS500

Figure 3. Evolution of total particle concentration (size 28-10000 nm) in the experimental chamber measured with the electrical low pressure impactor. a) Particle concentration, b) Comparison of DMS500 (size range 28 – 1000 nm) and ELPI measurements in test 1.

CPC measurement was above maximum limit value (> 10^5 particle·cm^{-3}). At this high level, coincidence effects occur and particle concentration is underestimated. OPC measurement showed a small peak of 2-3 particule·cm^{-3} (> 0.3 µm) at the ignition of the heater and no significant level afterwards.

The total particle emission rate was estimated using data from the differential mobility spectrometer. Considering the high air exchange rate in the experimental chamber, no significant coagulation or condensation was assumed to occur. Total decay rate was assumed to be a constant first order process. The total decay rate determined experimentally when the

heater is turned off was 84.8±4.7 h^{-1} (r^2 = 0.998) and verified the previous hypothesis. This value is higher than the air exchange rate which means that deposition of particles also occurs. Considering a surface to volume ratio of 4.59 $m^2 \cdot m^{-3}$ in the experimental chamber (including space heater), a deposition velocity of 2.3×10^{-3} $m \cdot s^{-1}$ can be estimated. With these assumptions, the evolution of concentration during the heater operation is given by the following equation:

$$\frac{dC_{(t)}}{dt} = \frac{E_{(t)}}{V} - \lambda C_{(t)} \quad (1)$$

where $C_{(t)}$ is the concentration of particles at time t (cm^{-3}), $E_{(t)}$ the total particle emission rate at time t (s^{-1}), V the volume of the experimental chamber and λ the total first order decay rate including air exchange rate and particle deposition (s^{-1}).

The total number of particles emitted during the heater operation N_{Total} is obtained by integrating instantaneous emission $E_{(t)}$ over the activity duration from t_0 (heater turned on) to t_n (heater turned off). $E_{(t)}$ is given in equation (1). N_{Total} is described in equation (2). The last term is approximated using the trapezium method and as the time step (t_n-t_{n-1}) is constant, equation (2) can be simplified to equation (3). The average emission rate over the entire activity duration $\bar{E}$ is then given by equation (4).

$$N_{Total} = \int_{t_0}^{t_n} E_{(t)}\, dt = V \int_{t_0}^{t_n} \frac{dC_{(t)}}{dt}\, dt + \lambda V \int_{t_0}^{t_n} C_{(t)}\, dt \quad (2)$$

$$N_{Total} \cong V(C_{t_n} - C_{t_0}) + \lambda V \frac{(t_n - t_{n-1})}{2} \sum_{t_1}^{t_n} \left(C_{t_n} + C_{t_{n-1}}\right) \quad (3)$$

$$\overline{E} = \frac{N_{Total}}{(t_n - t_0)} \quad (4)$$

The calculated emission rate was 1.77×10^{11} particle$\cdot s^{-1}$ with a relative standard deviation of 16% (n=3) for particles in the size range of 5 to 1000 nm. The source strength expressed as the total number of emitted particles in a given time was 4.25×10^{14} particles in 40 min.

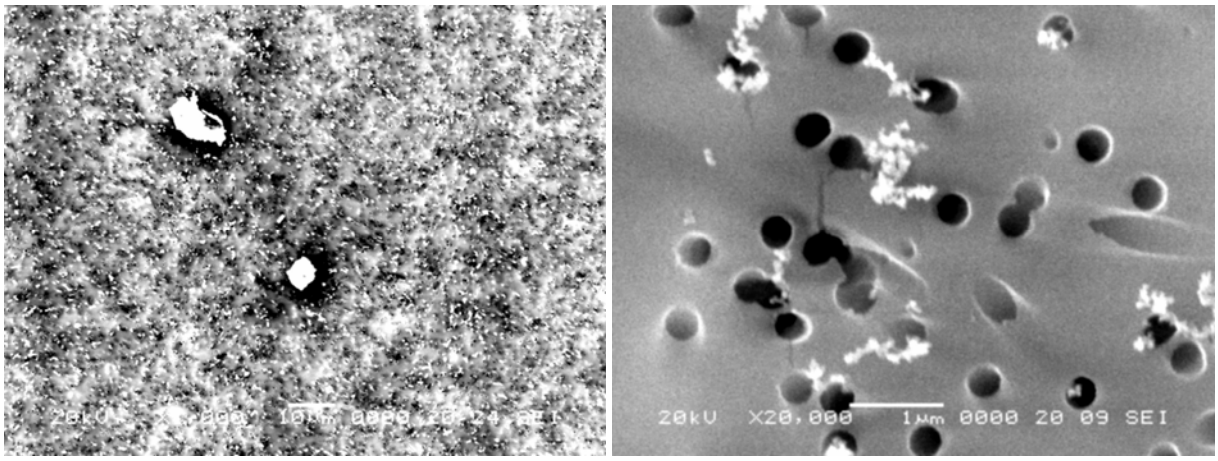
Chemical analysis

Despite the repetition of heating cycles, a limited mass of particles was collected on each filter. Therefore, a majority of measurements remained below detection limits or blank filter values. Nevertheless, PIXE analysis in the submicronic fraction showed important specific levels of chromium (628 ng$\cdot m^{-3}$ that corresponds to 4 ng$\cdot g^{-1}$ of burned fuel) and manganese (8 ng$\cdot m^{-3}$ equivalent to 0.05 ng$\cdot g^{-1}$ of burned fuel), compared to other tested indoor particle sources (Table 1). High concentration of other elements (particularly Al and Si) was also observed but at lower levels than other tested sources (not presented here). Both organic and elemental carbon were below detection limit of 28 ng$\cdot g^{-1}$. Trace levels of both sulfates and nitrates were found at 6 ng$\cdot g^{-1}$ of burned fuel. Other anions and cations were below detection limit. Significant levels of phenantrene (0.09 ng$\cdot g^{-1}$) and fluoranthene (0.015 ng$\cdot g^{-1}$) were also observed in the 1-2.5 µm fraction. Other PAHs were below detection limit.

Table 1. Concentration of elements ($ng \cdot m^{-3}$) measured by PIXE in the experimental chamber.

Fraction	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**
> 10 µm	96	285	30	3	3	< 1	< 11
2.5 - 10 µm	80	250	37	5	5	3	< 11
1 - 2.5 µm	86	185	33	1	1	< 1	< 11
< 1 µm	387	371	139	87	58	15	68
Fraction	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**Br**
> 10 µm	1.63	1.00	1.16	0.17	1.71	< 0.09	5.70
2.5 - 10 µm	4.26	0.40	1.72	0.26	< 0.09	< 0.09	5.17
1 - 2.5 µm	6.64	0.15	3.10	0.45	< 0.09	< 0.09	6.48
< 1 µm	627.53	8.29	12.53	3.85	< 0.60	3.98	43.02

Scanning electron microscopy showed a majority of aggregates < 1 µm formed by nanometric particles (microsoot) and a few coarse particles (Figure 4). Individual chemical analysis by energy dispersive X-ray spectrometry of these agglomerates revealed systematic presence of carbon and traces of silicon. On the other hand, the selected coarse particles were mostly composed of calcium as a major element. Other elements were not detected because of the lack of sensitivity in comparison with PIXE analysis.



a) SEM micrograph (x 1,000) b) SEM micrograph (x 20,000)

Figure 4. SEM micrographs of particles (in white) collected from kerosene space heater. Black spots represent filter pores, a) SEM micrograph x 1,000, b) SEM micrograph x 20,000.

DISCUSSION

Test conditions in the experimental chamber are focused on combustion particle characterization without any interaction from background particles. It does not simulate a real environment where air exchange rate and air velocity are typically low and surface deposition plays a critical role. Data presented in this paper are to be considered as primary emission as particle-particle and surface-particle interactions are restricted and thus particles in the nucleation mode are favoured. Some interactions were observed in the chamber when the heater is turned off and the air temperature decreases. The CMD growed from 9.5 to 14 nm, assumed to be caused by condensation of semi-volatile compounds. In order to transpose these data to a real environment, coagulation and condensation effects need to be taken into account. Experiments are currently being conducted in real environment to assess this point.

The deposition velocity found in this study is higher than typical values reported by Lai (2002) due to specific flow conditions in the experimental chamber. However, few deposition data about nanometric particles are available.

The particle emission rate of kerosene space heater is high compared to other reported indoor sources tested in experimental chambers (maximum of 1.5×10^{10} particle·s^{-1} for electric radiators, Afshari et al., 2005) or in real houses (up to 10^{10} s^{-1} for cooking activities, He et al., 2004, Hussein et al., 2006). Recently, particle emission rates up to 2.7×10^{11} particle·s^{-1} were reported for some laser printers in offices (He et al., 2007). It should be noted that the emission rate in this study covers particles down to 5 nm in diameter. When considering particles with a diameter above 10 nm, the emission rate becomes 8×10^{10} particle·s^{-1}. Size range of instruments must be taken into account to appropriately compare emission rates.

The dynamic conditions used in the experimental chamber were appropriate to characterize particle number concentrations as measuring instruments operate well in moderately high levels. These were however not completely compatible with the high mass loading needed to perform chemical analysis. Adding the fact that collecting particles on different size fractions also decreases cumulated mass per filter, a great number of analyses remained below detection limit. Nevertheless, significant results were obtained by PIXE and SEM. Current work in our laboratory on several other indoor activities (cooking, candles, incense smoke, sprays) showed that chromium and manganese are specific of the kerosene space heater. Sexton et al. (1986) identified also Cr, S and Si in kerosene heater emissions. Morawska and Zhang (2002) associated chromium with coal combustion. Leaderer et al. (1990, 1994, 1999) do not report chromium but rather associated kerosene space heaters with sulfur (mainly sulfates). In outdoor air, chromium is mainly associated to traffic proximity and industrial sectors (Nerriere et al., 2007). Chromium is occasionally or rarely found in urban homes (Van Winkle and Scheff, 2001).

CONCLUSIONS

Kerosene space heaters have been improved over years to limit pollutants by increasing combustion efficiency. They have no significant impact on the mass fraction of the aerosol but still represent a constant and major source of ultrafine particles (CMD = 9.5 nm) that can significantly affect indoor air quality. An extended duration of use may result in an important impact on occupant's exposure. The study still needs to take into account differences between heater devices and fuel type.

Presence of portable kerosene heaters was reported in only 3% of investigated dwellings during the French national indoor air survey that occurred from 2003 to 2005 (Kirchner et al., 2007). However, their frequency of use vary from region to region (northern and southern France) and also depends on the social and professional category of occupants. The occurrence in dwellings remains quite low but is increasing with heating energy costs.

ACKNOWLEDGEMENTS

This study is part of a project that receives financial support from PRIMEQUAL-PREDIT (French national research programme on air quality) and the French Ministry of the Environment and Sustainable Development. The authors would like to thank Céline Cannier for her investment in SEM analysis and Jean-Paul Lucas for mathematical suggestions. The authors are also grateful to Arnaud Noirtin from Intertek ICS, Chris Nickolaus from Cambustion Ltd and David Le Dur from Ecomesure for their help with the measuring instruments.

REFERENCES

Afshari A., Matson U., and Ekberg L.E. 2005. Characterization of indoor sources of fine and ultrafine particles: a study conducted in a full-scale chamber, *Indoor Air*, 15, 141-150.

Baron P. and Willeke K. 2001. Aerosol measurement. Principles, techniques and applications, 2nd Edition, Wiley-interscience, New York, 1131 pages.

Berwick M, Leaderer B.P., Stolwijk J.A., and Zagraniski R.T. 1989. Lower respiratory symptoms in children exposed to nitrogen dioxide from unvented combustion sources. *Environment International*, 15, 369-373.

He C., Morawska L., Hitchins J., and Gilbert D. 2004. Contribution from indoor sources to particle number and mass concentrations in residential houses, *Atmospheric Environment*, 38, 3405-3415.

He C., Morawska L., and Taplin L. 2007. Particle emission characteristics of office printers, *Environmental Science & Technology*, 41, 6039-6045.

Hussein T., Glytsos T., Ondracek J., Dohanyosova P., Zdimal V., Hämeri K., Lazaridis M., Smolik J., and Kulmala M. 2006. Particle size characterization and emission rates during indoor activities in house, *Atmospheric Environment*, 40, 4285-4307.

Johansson S.A.E., Campbell J.L., and Malqvist K.G. 1995. Particle-induced X-ray emission spectroscopy (PIXE), New York: Wiley.

Kirchner S., Arenes J.F., Cochet C., Derbez M., Duboudin C., Elias P., Gregoire A., Jedor B., Lucas J.P., Pasquier N., Pigneret M., and Ramalho O. 2007. Indoor air quality in French housing. *Environnement, Risques & Santé*, 6(4), 259-269. (*in French*).

Lai A.C.K. 2002. Particle deposition indoors: a review, *Indoor Air*, 12(4), 211-214.

Leaderer B.P. 1982. Air pollutant from kerosene space heaters. *Science*, 218, 1113-1115.

Leaderer B.P., Boone P.M., and Hammond S.K. 1990. Total particle, sulfate, and acidic aerosol emissions from kerosene space heaters. *Environmental Science & Technology*, 24(6), 908-912.

Leaderer B.P., Koutrakis P., Briggs S.L.K., and Rizzuto J. 1994. The mass concentration and elemental composition of indoor aerosols in Suffolk and Onondaga counites, New York, *Indoor Air*, 4, 23-34.

Leaderer B.P., Naeher L., Jankun T., Belanger K., Holford T., Toth C., Sullivan J., Wolfson J.M., and Koutrakis P. 1999. Indoor, outdoor, and regional summer and winter concentrations of PM_{10}, $PM_{2.5}$, SO_4^{2-}, H^+, NH_4^+, NO_3^-, NH_3, and nitrous acid in homes with and without kerosene space heaters. *Environmental Health Perspectives.* 107, 223-231.

Morawska L. and Zhang J.J. 2002. Combustion sources of particles.1. Health relevance and source signatures, *Chemosphere*, 49, 1045-1058.

Nerriere E., Guegan H., Bordigoni B., Hautemaniere A., Momas I., Ladner J., Target A., Lameloise P., Delmas V., Personnaz M.B., Koutrakis P., and Zmirou-Navier D. 2007. Spatial heterogeneity of personal exposure to airborne metals in French urban areas, *Science of the Total Environment*, 373, 49-56.

Sexton K., Webber L.M., Hayward S.B., and Sextro R.G. 1986. Characterization of particle composition, organic vapor constituents, and mutagenicity of indoor air pollutant emissions, *Environment International,* 12, 351-362.

Traynor G.W., Allen J.R., Apte M.G., Girman J.R., Hollowell C.D., 1983. Pollutant emissions from portable kerosene-fired space heaters. *Environmental Science and Technology*, 17, 369-371.

Van Winkle M.R. and Scheff P.A. 2001. Volatile organic compounds, polycyclic aromatic hydrocarbons and elements in the air of ten urban homes, *Indoor Air*, 11, 49-64.